

## PATENT ABSTRACTS OF JAPAN

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### (54) SELF-RETAINING POROUS SILICA AND ITS PRODUCTION

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a copolymer excellent in transparency and self-retaining properties, capable of presenting porous silica having a high specific surface area and useful for minute molecule-permeable materials, optical catalysts, catalyst carriers, etc., by polymerizing a mixture of specific silane compounds in the presence of a surfactant.

SOLUTION: This production of self-retaining porous silica is to copolymerize (B) a tetraalkoxysilane [e.g., the alkoxy is a 1-5C (branched) alkoxy] with (C) an alkenyltrialkoxysilane [e.g. the alkoxy is a 1-5C (branched) alkoxy and the alkenyl is a 2-5C (branched) alkenyl] in the presence of (A) a surfactant [e.g. a 14-30C (branched) alkyltrimethylammonium chloride]. The copolymer is obtained, e.g. by using 0.05-0.5 mole times of the component A based on the sum total mole number of the components B and C and copolycondensing them in the presence of water in an acidic condition. The objective porous silica is obtained by baking the copolymer and removing the component A.

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Notes:

1. Untranslatable words are replaced with asterisks (\*\*\*\*).
2. Texts in the figures are not translated and shown as it is.

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## CLAIMS

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### [Claim(s)]

[Claim 1] The copolymer which makes tetra-alkoxysilane and alkenyl trialkoxysilane come to polymerize under existence of a surface active agent.

[Claim 2] The copolymer according to claim 1 whose surface active agent is an alkyl trimethylammonium salt.

[Claim 3] The copolymer according to claim 1 or 2 which is self holding nature in porosity.

[Claim 4] Porosity silica material which consists of a copolymer according to claim 1, 2, or 3.

[Claim 5] Porosity silica material according to claim 4 which is a self holding nature film.

[Claim 6] The manufacture method of the copolymer of the porosity tetra-alkoxysilane and alkenyl trialkoxysilane which consist of carrying out copolycondensation of tetra-alkoxysilane and the alkenyl trialkoxysilane, and subsequently calcinating this under existence of a surface active agent.

## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

#### [0001]

[Field of the Invention] This invention relates to the new Silang copolymer. In detail, this invention is a copolymer which makes tetra-alkoxysilane and alkenyl trialkoxysilane come to polymerize under existence of a surface active agent, and relates to porosity silica of the high specific surface area excellent in self holding nature.

#### [0002]

[Description of the Prior Art] Although small molecules, such as molecule-like water and air, can be penetrated, let material which has the micropore of the nano size that a big object cannot be penetrated be the coating material of clothes or a packaging medium like liquefied water. Moreover, the material which has the micropore of nano size is used for the packaging

material, the sheet, etc. as a material of air, especially oxygen permeability. Many characteristics in connection with the permeability of a minute molecule in these minute molecule permeable materials, such as not only porosity but transparency and self holding nature, are demanded. Moreover, taking advantage of a sensor, catalyst support, especially transparency, it is applied also as a photocatalyst.

[0003] this invention person under existence of a surface active agent alkyl trimethylammonium salt Tetrafunctional alkoxysilane like tetramethoxy silane or tetra-ethoxy silane is hydrolyzed. A Thilly power surface active agent meso Mr. \*\* object is acquired for the transparent thin film about thickness 1mm by group Sakagami by carrying out the spin coat of the solution obtained by polymerizing on a substrate. It already finds out that the silica material of the porosity of nano size is obtained by calcinating this in the air and removing a surface active agent. It came (M. Ogawa, J.Am.Chem.Soc., 116, 7941; (1994) M.Ogawa, Chem.Comm., and 1149 (1996)).

[0004] However, the membranous self holding nature of the polymer obtained by this well-known method is inadequate, and a problem is in membranous handling nature, and it has been the hindrance of utilization.

[0005]

[Problem(s) to be Solved by the Invention] This invention aims at offering the silica material of the porosity excellent not only in porosity or transparency but self holding nature.

[0006]

[Means for solving problem] This invention relates to the copolymer which makes tetra-alkoxysilane and alkenyl trialkoxysilane come to polymerize under existence of a surface active agent, the becoming porosity silica material, and the silica material which is a self holding nature film. As a surface active agent used for this invention, an alkyl trimethylammonium salt is desirable. Moreover, the copolymer of this invention is characterized by being self holding nature by porosity. Furthermore, this invention carries out copolycondensation of tetra-alkoxysilane and the alkenyl trialkoxysilane under existence of a surface active agent, and relates to the manufacture method of the copolymer of the porosity tetra-alkoxysilane and alkenyl trialkoxysilane which consist of subsequently calcinating this.

[0007] as the alkoxy group of the tetra-alkoxysilane used by this invention -- carbon numbers 1-15 -- desirable -- 1 to 10 -- it is the shape of a normal chain or the letter alkoxy group of branching of 1 to 5 more preferably, for example, a methoxy group, an ethoxy group, a propoxy group, etc. are mentioned. Four alkoxy groups of the tetra-alkoxysilane of this invention may be the same, and although you may differ mutually, what has the same alkoxy group is desirable. Moreover, as for the tetra-alkoxysilane of this invention, some or all of the alkoxy group may be displacement or an unsubstituted phenoxy group. As tetra-alkoxysilane of this invention, there are tetramethoxy silane (TMOS), tetra-ethoxy silane, tetra-propoxysilane,

dimethoxy diethoxysilane, etc., for example.

[0008] The alkoxy group of the alkenyl trialkoxysilane used by this invention is good at the above mentioned alkoxy group, and these alkoxy groups may be the same or may differ mutually. moreover -- as the alkenyl machine of alkenyl trialkoxysilane -- carbon numbers 2-15 -- desirable -- 2 to 10 -- it is the shape of a normal chain of 2 to 5, or a letter alkenyl machine of branching more preferably, for example, a vinyl group, 1-propylene machine, 1-butylene group, etc. are mentioned. The number of the alkoxy groups of the alkenyl trialkoxysilane of this invention does not need to be three, you may be two pieces, and some or all of an alkoxy group may be displacement or an unsubstituted phenoxy group. As alkenyl trialkoxysilane of this invention Vinyltrimetoxysilane (VTMOS), vinyltriethoxysilane, vinyl tripropoxy silane, 1-propylene trimethoxysilane, 1-propylene triethoxysilane, 1-propylene tripropoxy silane, vinyl dimethoxy ethoxy silane, etc. are mentioned.

[0009] The amount of the alkenyl trialkoxysilane used of this invention is below an equivalent amount of tetra-alkoxysilane, and 0.01-0.8mol of alkenyl trialkoxysilane is 0.1-0.5mol more preferably to 1mol of tetra-alkoxysilane.

[0010] As a surface active agent used by this invention, if the copolycondensation of tetra-alkoxysilane and the alkenyl trialkoxysilane can be carried out, there will be no restriction in particular. This is because the surface active agent which existed at the time of a polymerization reaction will be removed, when calcinating the copolymer obtained at this polymerization reaction. However, since it seems that it is dependent on the kind and size of a surface active agent which are used at a polymerization reaction, the ordered structure of the obtained copolymer needs to choose a surface active agent according to the ordered structure made into the purpose, so that it may mention later.

[0011] As a surface active agent used for such the purpose, tetra-alkyl ammonium salt is desirable. as the alkyl group of tetra-alkyl ammonium salt -- carbon numbers 1-30 -- it may be the shape of a normal chain or the letter alkyl group of branching of 1 to 20 preferably, and four alkyl groups may be the same, and although you may differ mutually, an alkyl bird methyl object is desirable. the alkyl group of an alkyl trimethylammonium salt -- 14 or more carbon numbers -- the thing of a long chain is comparatively desirable. Although halogen ions, such as a chlorine ion and a bromine ion, are desirable as a counter ion of the tetra-alkyl ammonium salt of a surface active agent, it is not limited to these. as the tetra-alkyl ammonium salt of a surface active agent -- a tetra-deca nil trimethylammonium chloride -- it passes and a KISADE sill trimethylammonium chloride, an octadecanyl trimethylammonium chloride, an eicosanyl trimethylammonium chloride, etc. are mentioned.

[0012] To the sum total number of moles of tetra-alkoxysilane and alkenyl trialkoxysilane, 0.05-0.5mol of the amount of the surface active agent used of this invention is not limited in particular, although it is 0.1-0.3mol preferably.

[0013] The copolymer of the tetra-alkoxysilane of this invention and alkenyl trialkoxysilane can carry out copolycondensation of tetra-alkoxysilane and the alkenyl trialkoxysilane under existence of a surface active agent, and can be manufactured by subsequently calcinating this. A copolycondensation reaction is performed under existence of water. good [ on condition of the usual hydrolysis ] as reaction conditions -- reaction temperature -- the boiling point temperature of a room temperature to a solvent -- it is about 80 degrees C from a room temperature preferably. pH should just be an acidity side. Although it is not necessary to use a solvent in particular other than water, the organic solvent which can be mixed with water can also be used together.

[0014] The solution obtained by the copolymerization reaction is preferably developed in the shape of a sheet, and it dries by the usual method. Although it can also be based on the usual shaping method as a method of developing in the shape of a sheet, when manufacturing especially a thin film, the method of calling at a spin coat can also be taken. Then, the obtained dry matter is calcinated. Although calcination can be performed in the air, it is not limited to this. If it is the temperature from which the surface active agent which existed in reaction time is removed as a burning temperature, there will be no restriction in particular, but 250 degrees C or more are 300 degrees C or more preferably.

[0015] The copolymer of this invention is transparent and is the meso structure of self holding nature. One diffraction peak is looked at by the low angle in an X diffraction pattern. Drawing 1 as a surface active agent An octadecanyl trimethylammonium chloride (C18TAC) ((a) in drawing 1 ), Pass and A KISADE sill trimethylammonium chloride (C16TAC) ((b) in drawing 1 ), It is the X diffraction pattern of the copolymer of this invention manufactured using the tetra-deca nil trimethylammonium chloride (C14TAC) ((c) in drawing 1 ), and the dodecanyl trimethylammonium chloride (C12TAC) ((d) in drawing 1 ). d value acquired from this X diffraction pattern changed depending on the alkyl chain length of the used surface active agent, and were 3.63, 3.34, and 3.20nm, respectively at the time of C18TAC, C16TAC, and C14TAC (refer to drawing 2 ). Drawing 2 shows d value acquired from the X diffraction pattern, the black triangle mark is d value before the calcination at the time of using each surface active agent, and the black square mark shows d value after calcination. Moreover, the form even with after [ macroscopic ] removal of the surface active agent by calcination was held, and, as for the peak in an X diffraction pattern, it turned out that it remains and ordered structure is maintained.

[0016] It was shown that the surface active agent used for polymerization reaction time has contributed the meso structure of the copolymer of this invention to formation of ordered structure. As opposed to it having been difficult the thing for idea \*\* to obtain the film of self holding nature by the conventional system which uses tetramethoxy silane (TMOS) independently, if ordered structure is formed with volatilization of a solvent by the method of

this invention The meso structure film of self holding nature was obtained by adding trifunctional vinyltrimetoxysilane (VTMOS). It was unexpected although it was thought that this cause was because the gelling velocity of a product becomes slow by adding trifunctional vinyltrimetoxysilane (VTMOS).

[0017] Drawing 3 shows the Fourier transform infrared spectrum (FTIR) of the copolymer of this invention. [ (a) in drawing 2  $R > 2$ , (b), (c), and (d) ] Like aforementioned drawing 1, as a surface active agent An octadecanyl trimethylammonium chloride (C18TAC) ((a) in drawing 2), Pass and A KISADE sill trimethylammonium chloride (C16TAC) ((b) in drawing 2), The copolymer of this invention manufactured using the tetra-deca nil trimethylammonium chloride (C14TAC) ((c) in drawing 2) and the dodecanyl trimethylammonium chloride (C12TAC) ((d) in drawing 2) is shown.

[0018] Drawing 4 shows the thermogravimetric analysis (TG) and the differential thermal analysis (DTA) of a copolymer of this invention which were manufactured as a surface active agent using the octadecanyl trimethylammonium chloride (C18TAC).

[0019] This invention is excellent in transparency and self holding nature, offers the Thilly power copolymer of the porosity of high specific surface area, and offers a filmy or material useful as sheet-like mold goods especially.

[0020]

[Working example] Next, although an example explains this invention, this invention is not limited to these examples.

[0021] Example 1 tetramethoxy silane (TMOS) 1g (3mol (molar ratio)), putting in Vinyltrimetoxysilane (VTMOS) 0.325g (1mol (basis molar ratio)) underwater -- the inside of this -- 0.350g (0.5mol (molar ratio)) of hexadecyl trimethylammonium chlorides (C16TAC) -- in addition, it was made acidity with hydrochloric acid ( $\text{pH} < 1$ ). This mixture was made to react at 20 degrees C, and the uniform solution was obtained. It developed on the substrate, the obtained uniform solution was dried at 60 degrees C for 24 hours, and the target copolymer was obtained. The copolymer from which this was calcinated 550 degrees C in the air for 5 hours, and the surface active agent was removed was obtained. A Fourier transform infrared spectrum (FTIR) is shown in drawing 3 ((a) in drawing 3), and thermogravimetric analysis (TG) and a differential thermal analysis (DTA) are shown for the X diffraction pattern of the obtained copolymer in drawing 1 ((a) in drawing 1) at drawing 4. The obtained copolymer was excellent in porosity at self holding nature.

[0022] The surface active agent used example 2 was replaced with the hexadecyl trimethylammonium chloride of an example 1, and the copolymer was obtained like the example 1 using the octadecyl trimethylammonium chloride (C18TAC). The X diffraction pattern of the obtained copolymer is shown in drawing 1 ((b) in drawing 1), and a Fourier transform infrared spectrum (FTIR) is shown in drawing 3 ((b) in drawing 3). The obtained

copolymer was excellent in porosity at self holding nature.

[0023] The surface active agent used example 3 was replaced with the hexadecyl trimethylammonium chloride of an example 1, and the copolymer was obtained like the example 1 using the tetra-deca nil trimethylammonium chloride (C14TAC). The X diffraction pattern of the obtained copolymer is shown in drawing 1 ((c) in drawing 1 ), and a Fourier transform infrared spectrum (FTIR) is shown in drawing 3 ((c) in drawing 3 ). The obtained copolymer was excellent in porosity at self holding nature.

[0024] The surface active agent used example 4 was replaced with the hexadecyl trimethylammonium chloride of an example 1, and the copolymer was obtained like the example 1 using the dodecanyl trimethylammonium chloride (C12TAC). The X diffraction pattern of the obtained copolymer is shown in drawing 1 ((d) in drawing 1 ), and a Fourier transform infrared spectrum (FTIR) is shown in drawing 3 ((d) in drawing 3 ). The obtained copolymer was excellent in porosity at self holding nature.

[0025]

[Effect of the Invention] This invention is excellent in transparency and self holding nature, offers the Thilly power copolymer of the porosity of high specific surface area, and offers a filmy or material useful as sheet-like mold goods especially.

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[Translation done.]